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RADIOCHEMICAL DETERMINATION OF PLUTONIUM IN SEA WATER, SEDIMENTS AND MARINE ORGANISMS

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(Received 7th May 1971)

Various procedures are available for the determination of plutonium in aqueous samples, sediments and biological organisms. However, none is really adequate for low-level analysis because they have either low sensitivity or they are cumbersome for analysis of large samples.

In sea water analysis, the ion-exchange method¹ is suitable only for small volumes (5 l or less) and consequently the sensitivity is low for fall-out plutonium; the bismuth phosphate coprecipitation method² requires separation at temperatures of 80–100° which is impractical for processing samples of 50 l or more; and the iron(III) hydroxide method³ used to coprecipitate plutonium from 50–200 l samples at room temperature usually shows low recovery.

The procedure described in this paper is a modification of the iron(III) hydroxide method to separate plutonium from sea water by coprecipitation with iron(II) hydroxide and the recovery is significantly improved.

Of the many procedures available for separation of plutonium in soil and sediments^{4–8} and in biological samples^{9–11}, those involving complete dissolution usually give low sensitivity because only a small amount of sample can be processed conveniently. The leaching method⁷, which is capable of treating kilogram amounts of soil, is more suitable for low-level analysis. The leaching method, with nitric and hydrochloric acids, has been compared with the sodium carbonate fusion and the hydrofluoric–perchloric acid total dissolution methods¹² and the results showed no significant difference between methods of analysis for fall-out plutonium in several types of soil samples. Therefore this method was adopted for sediment analysis; it is also applicable to the analysis of biological samples after they have been dry-ashed.

EXPERIMENTAL

Reagents

All the reagents used were of reagent grade. All water was distilled and then deionized on a Dowex-50 cation-exchange column.

Iron carrier solution. 50 mg Fe^{3+} ml^{-1} in 0.5 M hydrochloric acid.

Plutonium-236 tracer. Standardized, 2–3 d.p.m. ml^{-1} in 1 M nitric acid. This need not be kept clean of ^{228}Th and other α -active daughters since the procedure

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provides good decontamination.

Anion-exchange resin. AG 1-X8, 100-200 mesh, Bio-Rad Lab., Richmond, Calif.

Counting apparatus

The α -spectrometer system consisted of an ORTEC 300 mm², 100- μ m depletion-depth, lithium-drifted silicon surface-barrier detector mounted in a chamber connected to a vacuum system, a detector bias supply (ORTEC Mod. No. 428), a FET preamplifier (ORTEC No. 109A), a power supply (ORTEC No. 115), a linear amplifier (Canberra No. 1416) and a 512-channel pulse-height analyzer (Nuclear Data No. 120) connected to a typewriter readout. With a scale expander (Canberra No. 1461), a 128-channel analyzer (Nuclear Data No. 110) may also be used.

Procedure for sea water

Sea-water samples of 50-60 l collected at depths of 0-700 m from the North Atlantic Ocean (1967-1969) contained sufficient ²³⁹Pu activity for convenient determination; however, much lower activity was observed for deeper samples¹³.

Clean thoroughly the sample barrel (top, side, handles, caps, etc.) of all dust, dirt and loose material. Weigh the sample in the original barrel and transfer the sea water to a polyethylene container of the appropriate size (100-300 l capacity). Weigh the empty barrel to determine the weight of the sample. Observe any unusual appearance in the sample (*e.g.* color, particulate matter, etc.). This information may be useful to establish contamination, if any, of the sample. Add *ca.* 500 ml of 3 M hydrochloric acid to the empty barrel, recap, rotate the barrel on its side a few times, and leave for at least 2-3 h. Combine the acid rinse with the sample. Rinse the empty barrel twice with about 1 l of deionized water and combine with the sample.

Add 10 ml of iron carrier and 1 ml of standardized plutonium-236 (2-3 d.p.m.) tracer. Stir the sample with tank nitrogen for about 1 h. Add 100 ml of 2 M sodium hydrogensulfite and stir with tank nitrogen for about 30 min. Add a second 100 ml of the sulfite solution and sufficient 15 M ammonia solution (300-400 ml) to make the solution basic; mix well. Cover the sample securely and allow the precipitate to settle overnight.

Carefully siphon off the main fraction of the supernate and transfer the hydroxide slurry to a 3-l beaker. Cover the beaker with aluminum foil or plastic wrap and let the hydroxide settle. Decant and centrifuge the remaining supernate. Dissolve the hydroxide with a minimal amount of 16 M nitric acid. Estimate the volume of the solution and add an equal volume of 16 M nitric acid. Transfer the solution to a 400-ml beaker and dilute the solution to *ca.* 100 ml with 8 M nitric acid. Add 5 ml of 30% hydrogen peroxide, cover the beaker with a watch glass, and heat on a hot plate at 90-100° until the peroxide has decomposed. Cool the sample to room temperature, add 1 g of solid sodium nitrite, mix, leave for 30 min and then proceed with the plutonium purification.

Procedure for sediments

Usually 50-100 g of dried shallow water sediments give sufficient fall-out ²³⁹Pu activity for convenient counting. Samples from the lower sections of cores (below 10 cm) or of oceanic sediments may require a larger aliquot; the ²³⁹Pu

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concentration in the 10-12 cm section of the core is usually about 1/10 the concentra-
tion of the surface section.

It was found that the addition of hydrochloric acid in the leaching step is
necessary only for sediment samples of low salinity. Most marine sediments contain
sufficient chloride for complete leaching of plutonium from the sample using only
nitric acid.

Weigh out a 100-g aliquot of dried sediment, transfer it to a 3-l beaker, wet the
sample with water, and add 1 ml of standardized plutonium-236 tracer. Carefully
add 200 ml of 16 M nitric acid and 100 ml of 12 M hydrochloric acid, slowly stir the
sample and allow the mixture to react at room temperature. If foaming becomes
appreciable, control it with the addition of a few drops of *n*-octanol. When the reaction
subsides, cover the beaker with a watch glass, heat gently, then to near boiling (90-100°)
and digest the sample for about 2 h with occasional stirring.

Add 300 ml of 1 M nitric acid and 25 ml of 30% hydrogen peroxide and continue
heating (90-100°) until the peroxide has decomposed. Cool the sample, filter through
a glass fiber filter paper and wash the residue with *ca.* 50 ml of hot 1 M nitric acid.
Transfer the residue back to the 3-l beaker and repeat the entire process from the
addition of concentrated nitric and hydrochloric acids. Combine the filtrate and acid
rinses and evaporate (90-100°) until salts begin to form. Estimate the volume of the
solution, add an equal volume of 1 M nitric acid, dilute to 1 l with 8 M nitric acid,
and cool to room temperature. Add *ca.* 10 g of solid sodium nitrite, mix and leave for
30 min before proceeding with the plutonium purification.

Procedure for marine organisms

The concentration of fall-out plutonium in marine organisms is quite variable;
a range from 0.004 d.p.m. kg⁻¹ in fish tissue to more than 10 d.p.m. kg⁻¹ in certain
seaweeds has been observed¹⁴. For optimal sample counting rate, the activity should
be about 0.5-5 d.p.m. Lower activity would require too long counting whereas higher
activity could unnecessarily increase the chance of cross-contamination between
samples.

Table I, which may be used as a guide for the selection of the proper sample
size, lists the average ²³⁹Pu concentrations in some marine organisms of the Atlantic
Ocean collected in 1970¹⁴. Similar ranges of ²³⁹Pu concentration have also been
found in some Pacific organisms¹⁵.

TABLE I

AVERAGE PLUTONIUM-239 CONCENTRATION OF MARINE ORGANISMS IN THE ATLANTIC OCEAN¹⁴

Organisms	²³⁹ Pu (d.p.m. per kg wet wt.)
Sargasso weed	13
Mixed Zooplankton	3
Starfish, <i>Asterias forbesi</i>	2
Mussels and clams, shell	0.6
meat	0.3
Fish, guts	0.9
bone	0.3
liver	0.1
meat	0.004

Weigh the wet organisms (dissected if necessary), take out the proper aliquot, dry to constant weight at 105° , and ash at $450-475^{\circ}$ until all the organic material has oxidized. Do not ash above 500° . Weigh the ash. Transfer the ash to a glass beaker. Since carbonates are formed during ashing, the initial reaction of the ash with acid is very vigorous; allow sufficient room in the selection of beaker so that spattering loss is minimized. Wet the ashed sample with water and add 1 ml of standardized plutonium-236 tracer. Proceed with the digestion and separation of plutonium as described in the procedure for sediments.

Plutonium purification procedure

Pass the sample solution obtained by the above steps through an anion-exchange column pre-conditioned with 8 M nitric acid. For sea-water samples, use 10 ml of wet resin in a 1-cm i.d. \times 20 cm column. and for sediment samples use 25 ml of wet resin in a 1.5-cm i.d. \times 30 cm column.

Allow the sample solution to drain to the top of the resin at a flow rate of about 10 ml min^{-1} . Using a 2-ml disposable glass pipet, rinse the column wall with 8 M nitric acid; drain the rinse solution carefully to the top of the resin. Repeat the rinse and draining step once. Elute the column with 30 ml of 8 M nitric acid, drain carefully to the top of the resin and discard the eluate. Elute as above with 30 ml of 12 M hydrochloric acid and discard this eluate.

Elute the plutonium with a solution of 30 ml of 16 M hydrochloric acid and 1 ml of 1 M ammonium iodide. Mix this eluant solution just before use. Collect the eluate in a 100-ml beaker, and evaporate below boiling to dryness on a hot plate. Remove the ammonium salts by evaporation with several portions of 2-3 ml each of 16 M nitric acid and 12 M hydrochloric acid. Rinse the wall of the beaker with each addition of acid. When the ammonium salts have evaporated, add a final rinse of 2-3 ml of 12 M hydrochloric acid, and evaporate the sample to dryness.

Add 5 ml of 12 M hydrochloric acid, warm the solution on a hot plate for a few minutes, and transfer to a 50-ml centrifuge tube. Rinse the beaker twice with 2-3 ml of 12 M hydrochloric acid and combine the solutions. Add ca. 100 mg of solid sodium nitrite, stir with a glass stirring rod, and allow to react for about 30 min. Centrifuge at low speed for 2-3 min. Transfer the supernate to the top of small ion-exchange column, loaded with 2 ml of wet AG 1-X8 resin preconditioned with 12 M hydrochloric acid. Drain the solution to the top of the resin, and rinse the tube and column walls twice with 1-ml portions of hydrochloric acid, draining carefully to the top of the resin each time. Wash the column with 20 ml of 12 M hydrochloric acid. Discard the eluate. Elute the plutonium with 20 ml of 12 M hydrochloric acid and 1 ml of 1 M ammonium iodide (mixed just before use).

Collect the plutonium eluant in a 50-ml beaker, and slowly evaporate to remove the ammonium salts as described above.

Electroplate the plutonium on stainless steel plating discs as described previously³, count, and resolve the activity by α -spectrometry.

RESULTS AND DISCUSSION

This procedure has routinely been inserted into the sequential scheme³ for analysis of fall-out radionuclides in sea water and other marine samples. The iron(II)

proper aliquot, the material has a glass beaker. Wash with acid to prevent spattering loss of plutonium as described

through an anion-exchange resin. For samples, use 25 ml

at a rate of about 1 ml/min. Wash with 8 M HCl. Repeat the rinse and drain carefully. Add 10 ml of 12 M

hydrochloric acid and heat. Collect the plutonium on a hot plate. Add 2–3 ml each of 12 M HCl. Wash with each and a final rinse of water.

Heat on a hot plate for a few minutes. Wash twice with 12 M HCl. Add ca. 100 mg of plutonium. Heat for about 30 min. Add a few drops of small ion-exchange resin. Wash with 12 M HCl. Add the tube and wash carefully to remove hydrochloric acid. Add 1 ml of 12 M HCl and 1 ml of 12 M HCl.

Evaporate to dryness.

As described

al scheme³ for plutonium. The iron(II)

hydroxide precipitation is made just after the removal of cesium with ammonium molybdophosphate (AMP); tests have shown that AMP carries no detectable plutonium from samples in the concentration range encountered.

The plutonium procedure requires 2–3 days for sediment or ashed organism samples and 3–4 days for sea water. In routine analysis two sets of 4 parallel samples can be processed in one week by a trained technician.

Sensitivity

The sensitivity of the procedure is respectively: 0.004 d.p.m. per 100 l of sea water (for a 50-l sample), 0.02 d.p.m. per kg of sediments (for 100 g of dried sediments), and 0.002 d.p.m. per kg (for 1 kg of fresh organisms); this is based on a two σ background uncertainty, a counting time of 48 h, and a counting efficiency of 38 %.

Chemical recovery

No radiochemical procedure in routine use today is quantitative for fall-out plutonium in large samples. Procedures based on "average" chemical yield from spiked analyses to correct for chemical loss are not reliable. Neither accidental nor intrinsic loss in such procedures can be accurately corrected. Therefore, cyclotron produced plutonium-236 tracer, free from other plutonium isotopes, is used in this laboratory for monitoring recovery of plutonium in analysis.

On thirty samples of 5–60 l of sea water, analyzed by the present procedure, the average plutonium recovery was 52 ± 18 %; even higher recoveries, up to 85 %, were obtained in the smaller volume samples. This compares to 25 ± 14 % (on 38 samples) by the iron(III) hydroxide method³.

The average recovery on 75 samples of sediments and ashed organisms was 63 ± 20 % (range 30–99 %) by the given leaching method. Changing the sample size between 50 and 400 g of dried sediments showed no systematic effect on the recovery.

A possible explanation for the low recovery in the iron(III) hydroxide procedure is that the plutonium is lost through the formation of plutonium(IV) polymers. Plutonium(IV) ions are known to form polymers very readily in many solutions at low acid concentrations^{5,16,17}. The chemical behavior of the polymers is significantly different from that of the ionic forms. Plutonium(IV) polymers are difficult to filter, extract, or coprecipitate because the size and charge of the colloidal particles vary unpredictably under many conditions.

This procedure avoids the difficulty encountered with plutonium(IV) polymers, by reduction of Pu(IV) to Pu(III) with sulfite and then separating the plutonium from sea water by coprecipitation with iron(II) hydroxide. Sodium hydrogensulfite or gaseous sulfur dioxide are both effective for the depolymerization and reduction of colloidal plutonium in acidic solution¹⁷.

Polymerization loss of plutonium in the analysis of sediments and organisms is small, if not negligible, because the sample solution is maintained at a high acid concentration throughout the procedure.

Absolute values

The data presented here were all normalized to the disintegration rate, corrected for radioactive decay, of a plutonium-236 solution calibrated at the Health and Safety Laboratory, USAEC, in June 1965. At present there is some uncertainty about the absolute value of this solution.

TABLE II
ANALYSIS OF SEA WATER

Sample no.	Location	Date	^{239}Pu (d.p.m. per 1000 kg) ^a	Std. dev.
228	27° 47' N 67° 35' W	Dec. 1968	1.5 ± 0.5	0.6
331	27° 47' N 67° 35' W	Dec. 1968	2.6 ± 0.5	
332	27° 47' N 67° 35' W	Dec. 1968	2.6 ± 0.7	
267	36° 23' N 70° 3' W	June 1969	2.6 ± 0.8	0.7
268	36° 23' N 70° 3' W	June 1969	2.3 ± 0.5	
269	36° 23' N 70° 3' W	June 1969	1.4 ± 0.2	
270	36° 23' N 70° 3' W	June 1969	3.1 ± 1.1	
389	WHOI Aquarium	Aug. 1970	2.9 ± 0.8	0.3
390	line	Aug. 1970	2.5 ± 0.4	
207	IAEA STD. 1	1970	123 ± 5	13
208	Seawater 1	1970	116 ± 5	
209	Seawater 1	1970	144 ± 8	
210	Seawater 1	1970	118 ± 6	
211	Seawater 2	1970	316 ± 18	11
212	Seawater 2	1970	298 ± 12	
213	Seawater 2	1970	324 ± 21	
214	Seawater 2	1970	313 ± 15	

^a The ± values are the 1 σ of the counting error.

TABLE III
ANALYSIS OF SEDIMENTS

Sample no.	Location	Date	^{239}Pu (d.p.m. per kg dry wt.) ^a	Std. dev.
13	Cape Cod, Mass.	1968	72 ± 7	6
13-R	Cape Cod, Mass.	1968	80 ± 2	
16	Cape Cod, Mass.	1968	82 ± 6	
16-R	Cape Cod, Mass.	1968	84 ± 2	
202	Bombay, India	1970	374 ± 15	7
203	Bombay, India	1970	389 ± 15	
204	Bombay, India	1970	374 ± 15	

^a The ± values are the 1 σ of the counting error.

Replicate analysis

Analyses of sea water, sediments and organisms are shown in Tables II-IV. The average standard deviation of the replicates is well within the 1 σ counting error of the samples (except for sea-water samples No. 207-210).

Contamination and blank activity

Little or no plutonium-239 contamination was found in reagent and simulated sea-water blanks (Table V). The simulated sea-water samples were obtained from deep oil well brine known to be free of fall-out radioactivities. The average ^{239}Pu concen-

TABLE IV
ANALYSIS OF ORGANISMS

Std. dev.	Sample no.	Organisms	^{239}Pu (d.p.m. per kg wet wt.) ^a	Std. dev.
0.6	27	Shark liver	0.28 ± 0.07	0.05
	41	Shark liver	0.21 ± 0.06	
	32	Shark bone	0.025 ± 0.012	0.007
0.7	32-R	Shark bone	0.035 ± 0.014	
	40	Blue mussels	0.33 ± 0.12	0.02
	57	Blue mussels	0.36 ± 0.05	

^a The \pm values are the 1σ of the counting error.TABLE V
PLUTONIUM-239 ACTIVITY IN REAGENT AND SIMULATED SEA-WATER BLANKS

Sample	^{239}Pu (d.p.m. per sample)
Reagent blanks	0.005 ± 0.005
	0.017 ± 0.015
	0.007 ± 0.007
Simulated sea-water blank	-0.005 ± 0.010
	0.010 ± 0.02
	-0.010 ± 0.02
Average	0.004 ± 0.010

tration of 6 such blanks (50 l), processed along with regular sea-water samples, was 0.004 ± 0.010 d.p.m. per sample, or about a factor of 2 above the detection limit.

The present detector background (5.00–5.20 MeV) for ^{239}Pu was less than one count per 24 h. The average detector background activity over an extended period of about 10,000 min was 4 counts, or 0.0004 ± 0.0002 c.p.m., near the region of the ^{239}Pu α -spectrum. Similar background activity was also found near the regions of the α -peaks of ^{238}Pu (5.30–5.50 MeV) and ^{236}Pu (5.60–5.80 MeV). This level of background activity is an exception rather than a general rule for most solid-state detectors. Much higher background has been observed in some solid-state detectors because of contamination with ^{241}Am used by the manufacturer for their calibration¹³. The present detectors were purchased from the manufacturer before any test with ^{241}Am . Such detectors are not hard to obtain, but the requirement must be explicitly specified to the manufacturer.

The average counting rate of the samples was about 0.5 c.p.m.; build-up of detector contamination from recoil atoms was negligible in about 15 months of operation. This is consistent with recoil studies of α -emitters with daughters of long half-lives such as the decay products of the plutonium isotopes¹⁸.

In the determination of plutonium-238, a serious decontamination problem was encountered. Figure 1 shows a typical α -spectrum of the major peaks of ^{236}Pu , ^{238}Pu and ^{239}Pu ; on this are superimposed the peaks, with the same detector and

geometry, of thorium-228, and radium-224 in this energy region. It is clear that ^{238}Pu , the least abundant of the plutonium isotopes measured, is seriously interfered with by ^{228}Th , which is present, as a decay product, in the ^{236}Pu tracer, as well as being very rich in most recent marine sediments, and detectable in marine organisms. Radium-224 is no problem in the method described since it does not follow plutonium in the hydroxide precipitation.

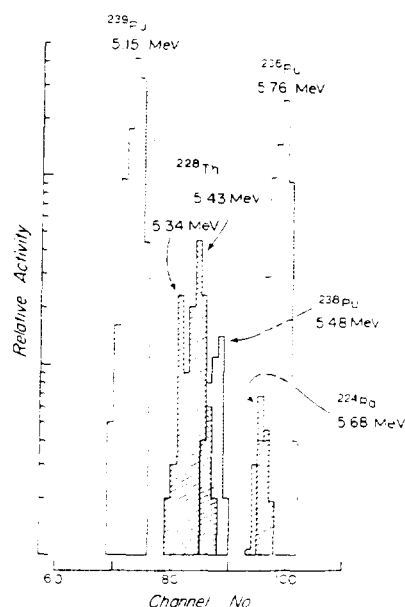


Fig. 1. α -Spectrum of ^{239}Pu , ^{238}Pu , ^{236}Pu , ^{228}Th and ^{224}Ra .

Thorium, however, does follow plutonium in the hydroxide precipitates and is not effectively cleaned up by the nitric acid elution (necessary for separation of iron from plutonium) on the anion-exchange column, nor, on this column, by hydrochloric acid elution: Stubborn traces of thorium continue to elute after many column-volumes of this acid. This is probably because of strong adsorption of thorium-nitrate complexes in the interstitial cavities of the resin beads, where the hydrochloric acid wash may be physically restricted. Use of a second anion column, equilibrated with hydrochloric acid, has proved necessary and effective: On this column plutonium adheres until eluted with hydrochloric acid-ammonium iodide whereas thorium is quickly washed out with concentrated acid.

Other parameters

Two kinds of material, platinum and stainless steel, were studied for the mounting of plutonium for α -spectrometry. Stainless steel discs were chosen because they are considerably less costly than platinum and the quality of the plated sample is not significantly different from that of the platinum disc in terms of both α -resolution and adhesion of plutonium to the plate.

The resolution of the spectrometer used for the 5.76-MeV α -emission of ^{236}Pu is 60 ± 5 keV (FWHM) on stainless steel discs as compared to 65 ± 5 keV for platinum

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discs. A plutonium-236 source electroplated on a stainless steel disc and used as a detector standard over a period of 32 months showed loss of neither activity (other than its normal decay) nor resolution.

Adsorption loss of plutonium on several laboratory wares was also checked. Known amounts of plutonium-236 standard were evaporated in Pyrex beakers, Teflon beakers, ceramic and Vycor crucibles with hydrochloric-nitric acid mixtures; the standard was then transferred to an electroplating apparatus, electroplated and counted. No significant difference was found in these standards from one that was directly electroplated.

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SUMMARY

A radiochemical procedure is described for the determination of plutonium in large samples of sea water, sediments and organisms with a sensitivity of 0.004 d.p.m. per 100 l of sea water (for a 50-l sample), 0.02 d.p.m. per kg of sediments (100-g sample) and 0.002 d.p.m. per kg of marine organisms (1-kg sample). An iron(II) hydroxide coprecipitation method is used for the concentration of plutonium in sea water. A nitric-hydrochloric acid leaching method is adapted for the treatment of sediments and ashed organisms. Factors influencing the recovery, contamination and blank activity are discussed.

RÉSUMÉ

Une méthode radiochimique est décrite pour le dosage du plutonium dans des échantillons d'eaux de mer, de sédiments et d'organismes marins, avec des sensibilités de 0.004 d.p.m./100 l (prise d'échantillon 50 l), 0.02 d.p.m./kg (prise de 100 g) et 0.002 d.p.m./kg (prise de 1 kg) respectivement. Le plutonium est concentré par coprécipitation avec l'hydroxyde de fer(II). Un traitement au mélange acide nitrique-acide chlorhydrique est proposé pour sédiments et cendres d'organismes. Divers paramètres sont examinés.

ZUSAMMENFASSUNG

Es wird ein radiochemisches Verfahren beschrieben, mit dem Plutonium in grossen Proben von Meerwasser, Sedimenten und Organismen mit einer Empfindlichkeit von 0.004 d.p.m./100 l in Meerwasser (bei einer 50 l-Probe), 0.02 d.p.m./kg in Sedimenten (100 g-Probe) und 0.002 d.p.m./kg in maritimen Organismen (1 kg-Probe) bestimmt werden kann. Für die Anreicherung des Plutoniums in Meerwasser wird eine Eisen(II)-hydroxid-Mitfällungsmethode angewendet. Sedimente und veraschte Organismen werden mit einem Gemisch von Salpeter- und Salzsäure ausgezogen. Die Faktoren, die den erfassten Anteil, die Kontamination und Blindaktivität beeinflussen, werden diskutiert.

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